FINAL PROJECT REPORT TO ONR

***In situ* Studies of Defect Nucleation During the PVT and CVD Growth of Silicon Carbide Single Crystals (N000140710485; January 2007 – April 2008)**

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The emphasis in this project was on in situ observation of defect nucleation processes by carrying out CVD homoepitaxial growth of 6H- and 4H-SiC growth in a chamber specially designed to enable synchrotron white beam X-ray topographic (SWBXT) *in situ* observation of the growing crystal, both bulk and surface regions. In addition a significant amount of *ex situ* topographic work was carried out on wafers sliced from boules grown in situ in the X-ray beam and boules not grown in situ in the X-ray beam. The growth system was set up using commercially procured gas flow controls and scrubber units, and integrating them with a modified in-house designed growth chamber that has options for *in situ* X-ray topographic study. The CVD system uses silicon tetrachloride ($SiCl_4$), silane (SiH_4), propane (C_3H_8), hydrogen (H_2) and argon (Ar) gases.

The hot-zone design and growth conditions were optimized by using numerical modeling as well as thermodynamic modeling. Detailed numerical modeling showed how the temperature field contours get shifted towards the exit end of the hot-zone depending on the associated thermal capacity of the gases at different flow rates. Detailed experiments were performed in both the kinetically and thermodynamically controlled regions, achieved by altering the growth parameters, and the results compared with our equilibrium model. This enabled it to be determined that kinetically controlled CVD growth is more effective, and that 6H-SiC homo-epitaxial layers grown at about 1500°C in this condition resulted in high quality films in terms of surface morphology and lower basal plane dislocation density.

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14. ABSTRACT

The emphasis in this project was on in situ observation of defect nucleation processes by carrying out CVD homoepitaxial growth of 6H- and 4H-SiC growth in a chamber specially designed to enable synchrotron white beam X-ray topographic (SWBXT) in situ observation of the growing crystal, both bulk and surface regions. In addition a significant amount of ex situ topographic work was carried out on wafers sliced from boules grown in situ in the X-ray beam and boules not grown in situ in the X-ray beam. The growth system was set up using commercially procured gas flow controls and scrubber units, and integrating them with a modified in-house designed growth chamber that has options for in situ X-ray topographic study. The CVD system uses silicon tetrachloride ($SiCl_4$), silane (SiH_4), propane (C_3H_8), hydrogen (H_2) and argon (Ar) gases.

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Thick films, up to 300 μm, of 6H SiC and 4H SiC could be grown using $SiCl_4$ and C_3H_8 precursors. *In situ* studies proved difficult, mostly complicated by the stringent safety requirements at the synchrotron source which are dictated by the Department of Energy. By far the most useful information was obtained in the *ex situ* work. The as-grown films have been subjected to various characterization procedures, in particular to the imaging of defects structure using X-ray topography and its variants. Grazing incidence and back reflection synchrotron X-ray topographs revealed basal plane dislocations, threading screw dislocations in the entire area of the epitaxial layer and the substrate. Low basal plane dislocation density ($10^4/cm^2$) was observed in the epitaxial layer grown at slower rates (e.g. 5μm/hr). Most of these basal plane dislocations show predominantly edge character. KOH etching carried out on the epitaxial layer revealed low angle grain boundaries that consisted predominantly of threading edge dislocations. The threading edge dislocations and threading screw dislocations densities were $10^4/cm^2$ and $10^3/cm^2$, respectively. Suitable steps were researched and implemented to lower dislocation densities. In general, defects present in the substrate such as micropipes, threading dislocations and grain boundaries are found to replicate in the epitaxial layer. However, no additional micropipe nucleation was observed in the epitaxial layer. Some elementary screw dislocations present in the substrate found to disappear in the epitaxial layer, evidently due to some kind of conversion and/or annihilation mechanism. Extensive SWBXT studies enabled the details of this conversion mechanism to be elucidated. According to this mechanism, which is shown schematically in Fig. 1, the spiral step configurations associated with the surface termination of the threading screw dislocations in the substrate are overgrown by fast moving vicinal steps during the CVD growth process. The screw dislocation does not have the opportunity to replicate itself during overgrowth and is forced to bend over into the basal plane creating a pair of Frank partial dislocations separated by a Frank fault. The Burgers vector of the Frank partials and the fault vector of the Frank fault were confirmed using **g.b** and **g.R** criteria as shown in figure 2. In addition, we also developed a geometrical model that clearly explains the conversion of basal plane dislocations into threading edge dislocations. Six types of threading edge dislocations were identified and confirmed using image simulation.

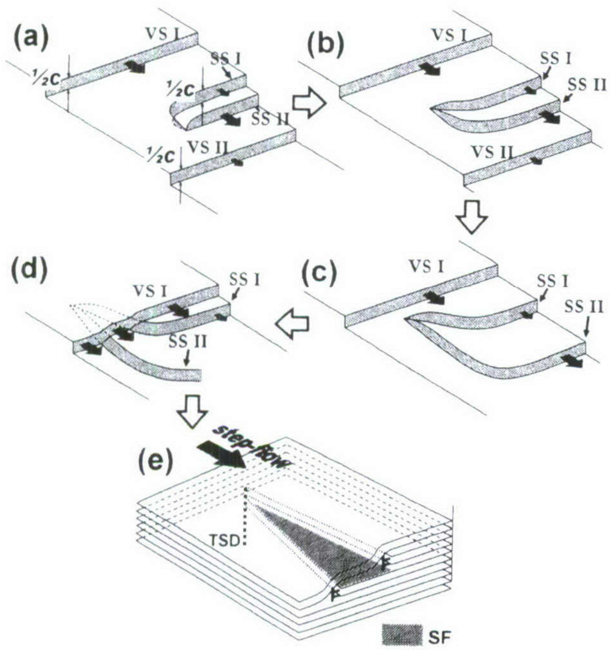

Figure 1. Mechanism for conversion of threading screw dislocations into pairs of Frank partial dislocations separated by a Frank Fault. Vicinal step VSI overgrows the spiral demi-steps SSI and SSII associated with the threading screw dislocation (TSD).

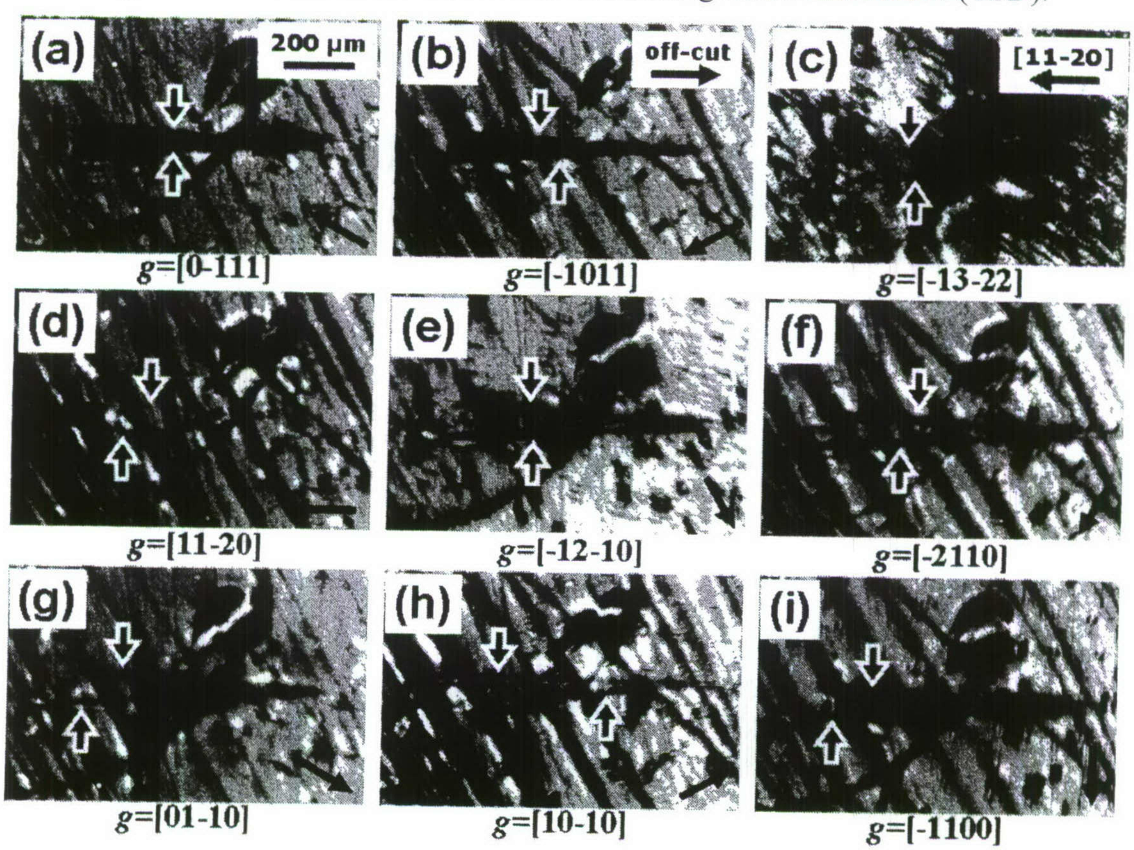

Figure 2. Fault and Burgers vector analysis of the Frank Partials and Faults.

The dislocation densities observed primarily depended on the substrate quality. The rocking curve measurements show that in certain cases that structural quality of the epitaxial layer was better than the original substrate when off-cut substrates were used. The growth rates were found to increase with the growth temperature. However, the growth rate reduced when the hydrogen flow rate was increased from 5 slpm to 15 slpm, which agrees well with our modeling. This effect also correlates well with the observation of shifting of the maximum temperature due to the gas flow effects from the modeling results. Good films, with superior surface quality containing lower dislocation density, were obtained at about 1500°C and above which the morphology becomes rough because of the simultaneously occurring hydrogen etching. A hydrogen defect etching process was developed to reveal micropipes and also obtain a quantitative measure of micropipes.

Optimization of the CVD system enabled it to be run reliably for 24 hour periods without any blockages occurring in the hot-zone. The system is suitable for growing mm size boules using halide precursors. While e*x situ* studies were so far more successful than in situ, routine *in situ* work requires investment in growth system elements with improved safety precautions and controls. The *in situ* work will undoubtedly provide insights into defect nucleation and the crystal growth processes not attainable in the *ex situ* work.

This ONR grant also resulted in manpower training. Two Ph.D students (Yi Chen MS, 2003, Ph.D, 2008; Ning Zhang, PhD estimated 2010) and a postdoc (Dr. G. Dhanaraj) were employed on this project.

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